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Photo-induced strengthening of weak bonding in noble gas dimers

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We demonstrate through extensive first-principles time-dependent density functional calculations that attractive van der Waals interaction between closed-shell atoms can be enhanced by light with constant spatial intensity. We illustrate this general phenomenon for a He dimer as a prototypical case of complex van der Waals interactions and show that when excited by light with a frequency close to the $1s \rightarrow 2p$ He-atomic transition, an attractive force larger than 7 pN is produced. This force gain is manifested as a larger acceleration of He-He contraction under an optical field. The concerted dynamical motions of the He atoms together with polarity switching of the charge-induced dipole cause the contraction of the dimer. These findings are relevant for the photo-induced control of weakly bonded molecular species, either in gas phase or in solution.
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Laser-induced optical manipulation of microparticles (the "optical tweezer effect") has motivated many studies[1,2] since it was first reported.[3] The strength of such interaction was theoretically predicted to depend on microparticle size.[4] Optical traps were scaled up from single atoms to diatomic molecules,[5] and the theoretical possibility of making atomic lattices by using optical fields was noted.[6] Recently, by using two orthogonal standing-wave lasers, the proposed optical lattice trap was experimentally realized.[7] Because controlling the spatial intensity profile of light is key to controlling ions, high precision trapping can be achieved by using photonic crystals made with recent advanced technologies[8–10] or otherwise by using nanoparticles that generate near-field plasmon[11] whose optical field has a steeper spatial gradient than the optical field of a laser.

In this work, we propose the photo-induced enhancement of interatomic attractive interaction even in the absence of the spatial intensity profile of light. The parameters of light that must be tuned to maximize the enhancement are only the frequency and direction of the polarization vector. The effect relies on a mechanism different from the one proposed for the optical tweezer effect.[3,4] The mechanism of enhancement can be intuitively understood in terms of the photo-induced attractive interaction between the coherently time-varying dipoles of each neutral atom; this is schematically depicted in Fig. 1. This interaction is similar to the London force in the absence of an optical field.[12] To maximize the dipole-dipole attraction, the amplitude of electron motion must be enhanced by light having sufficiently strong intensity and a frequency close to resonance with the photo-excitation energy of the particle.[13]

At the same time, the optical field should also cause electron excitation into anti-bonding molecular orbitals of these particles. Therefore, it is a technical challenge to persistently enhance the force by simply tuning photon energy, making theoretical evaluation of the feasibility of the enhancement a worthwhile endeavor.

To illustrate the microscopic mechanism of laser-induced attraction, we chose the simplest van der Waals interacting system, the He dimer, as a test case. Then we show that photo-induced enhancement of the attractive forces can be achieved with a tuned optical frequency. The He dimer is known to be weakly bound by van der Waals dispersion forces.[14,15] In all our calculations, we included dispersion forces following the scheme proposed in Ref. 16 (see the supplementary material[17] for details). We initiated the time-dependent density functional theory (TDDFT) electron-ion dynamics[18,19] by setting the He-He distance to 2.9 Å (i.e., very close to the theoretical optimum distance of

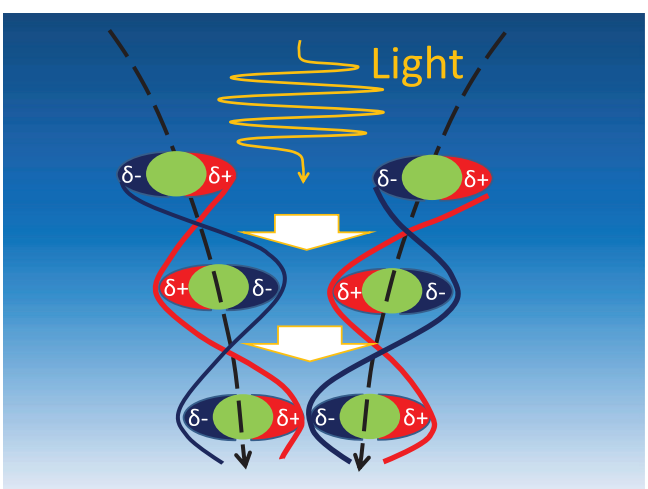

FIG. 1. Schematic of photo-induced attraction between two neutral particles. White arrows indicate the time axis and black dotted arrows indicate the trajectory of the two particles. The oscillation of each particle's dipole moment is represented by two curving lines for positively (red) and negatively (blue) redistributed charges.

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2.86 Å); we then applied an alternating electric field (E-field) polarized along the molecular axis with frequency of about 5.5×10^3 THz, which is close to the theoretical $1s \rightarrow 2p$ resonance excitation energy of a He atom (20 eV; see Fig. S1 (Ref. 17)), to be compared with the experimental value of 21.21 eV.[20] To avoid electron emission from He atoms, the strength of the E-field was set to 0.03 V/Å, giving a value for the Keldysh parameter of over 72.[21] This parameter value means that electron emission by tunneling is rare under the stated conditions. This E-field strength corresponds to laser power of 1.214×10^{10} W/cm^2, which is far below the experimental limit. (See, for example, Ref. 22 for photon energy similar to that in the present simulations.) We used a $10 \times 5 \times 5$ Å^3 box as a unit cell. Further, computational details of our first-principles TDDFT electron-ion dynamics are described in the supplementary material[17] and in the Refs. 23–28.

We computed the response of the He dimer to a short pulse with full width at half-maximum of 0.066 fs, polarized along the He-He axis, by evaluating the total dipole moment $\mathbf{P}(t) = \int \rho(\mathbf{r}, t)(\mathbf{r} - \mathbf{r}_0)d\mathbf{r}$.[29] The time evolution of $\mathbf{P}(t)$ was computed, which provides the frequency-dependent response function $\mathbf{P}(\omega)$[27,30] showing main transitions around 20 eV (see Fig. S2 (Ref. 17)). This energy is close to the atomic excitation energy of He obtained by TDDFT, as shown in Fig. S1.[17]

Once the full electronic response had been characterized, we computed the electron-ion dynamics of the He dimer with different applied optical fields with energies ranging from 19.89 to 20.32 eV. Figure 2(a) displays a summary of the computed electron dynamics: The total dipole moment $\mathbf{P}(t)$ exhibits either Rabi oscillation or continuously increasing amplitude, depending on the frequency of the applied field. The largest and smallest photon frequencies (Fig. 2(a)), with corresponding energies of 19.89 eV and 20.32 eV, respectively, produce detuned Rabi oscillation of total dipole moment. This detuned behavior should also emerge even when the frequency is in exact resonance with the excitation energy.[31] This result is expected for an isolated He atom; there is a dynamical detuning in the dipole response induced by the artificial adiabatic exchange-correlation functional (see Ref. 31 for more details). That is, the time-dependence introduced by varying the density on the adiabatic Kohn-Sham effective potential brings the system out of resonance even if at the initial time the applied frequency was resonant with one of the system excitations. Interestingly, we obtained a fast increase of the amplitude of the total dipole moment $\mathbf{P}(t)$, as displayed in middle of Fig. 2(a), when we set the frequency of photon energy at 20.00 eV.

Depending on the frequency of the applied field, we obtain a small enhancement to the attractive force between He atoms in the excited state molecular dynamics (MD) simulations within the TDDFT Ehrenfest framework.[32] Figure 2(b) compares the time course of the relative velocity of He-He contraction under an external optical field for energies ranging from 19.89 to 20.32 eV to the He-He dynamics in the absence of an optical field. By placing He atoms at the equilibrium distance with high precision, we should be able to monitor optically induced He-He contraction. To accentuate the photo-induced contraction process, we start from a slightly larger interatomic He distance, 2.90 Å, but the physical mechanism described here is independent of initial starting condition.[33] Within the simulation up to time 33 fs, photo-induced contraction of He dimer is evident for the photon energies considered here. Beyond time 33 fs, the TDGGA calculation can still guarantee numerical precision by using a smaller time step, and should be checked by the energy conservation rule.[28] Figure S3 (Ref. 17) shows longer-time results that still show He-He contraction.

The acceleration of the atoms was derived from the time evolution of the velocity (Fig. 2(b)). Within the current simulation time, the velocity error bars indicate precision of 1×10^{-7} atomic units (relative to the magnitude of velocity shown in Fig. 2(b)). Thus, the velocities exhibit notable differences between several photon energies. Among these cases, photon energy of 20.00 eV corresponds to consistently faster contraction than that in the simulated system without optical E-field (up to 33 fs). The estimated photo-enhanced attractive force at times from 23 fs to 33 fs at photon energy of 20.00 eV was around 7 pN.[34]

Figures 3(a) and 3(b) highlight the contrast in charge redistribution $\rho(\mathbf{r}, t = 28\,\text{fs}) - \rho(\mathbf{r}, t = 0)$ between cases with and without optical excitation. Figure 3(a) indicates He-He attraction without light driving electron accumulation in bonding He 1*s* orbitals. Such attraction is naturally understood as a consequence of the weak van der Waals interaction. The individual dipole moments of the two He atoms (with magnitude of $\sim 3 \times 10^{-4}$ atomic units) are oriented in opposite directions to maintain symmetry with respect to a mirror plane between the two He atoms. Thus, in this system the dipole-dipole attraction must be absent. In contrast, light

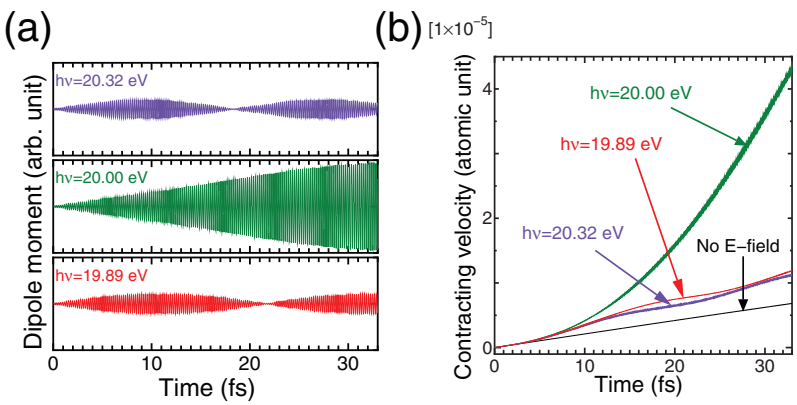

FIG. 2. (a) Time evolutions of the total dipole moment of He dimer driven by an E-field polarized along the dimer axis for several photon energies, and (b) time evolutions of the relative velocity of photo-induced He-He contraction for several photon energies. Positive velocity corresponds to He-He contraction.

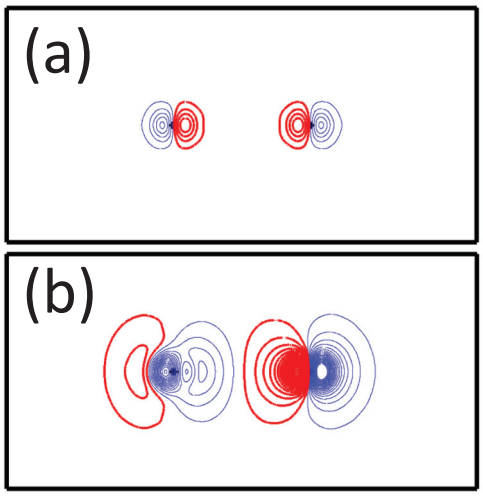

FIG. 3. Charge modulation ($\rho(\mathbf{r}, t) - \rho(\mathbf{r}, t_{=0})$) of He dimer at $t = 28.16$ fs (a) without optical field and (b) with optical field at photon energy of 20.00 eV. Thick (red) contour lines denote electrons; thin (blue) lines denote holes. Contour lines are drawn with intervals of $5.1 \times 10^{-4} e$ per Bohr,[3] where e represents the charge of a single electron.

with photon energy of 20.0 eV strengthens the oscillating individual dipole moments of He atoms in the same direction. This breaks the mirror symmetry, as shown in Fig. 3(b). The dipole moments have a magnitude of over 3×10^{-2} atomic units, two orders of magnitude larger than that in Fig. 3(a). This can thus give rise to considerable dipole-dipole attraction, corresponding to the schematic shown in Fig. 1. We therefore conclude that the optical enhancement of He-He attraction up to $t = 33$ fs is supported when the photon energy is near the $1s \rightarrow 2p$ excitation level.

From the viewpoint of molecular orbital theory, such excitation can be expected to promote an electron to a He-He anti-bonding orbital, which should cause He-He repulsion, in contrast to the simulation results. However, even though the optical frequency is close to resonance with that excitation, we found that the electronic excitation is insufficient to cause the $1s \rightarrow 2p$ optical transition. Figure 4 shows the computed increase in the He dimer's internal energy, which grows to 0.8 eV and then decreases much less than the photon energy 20.00 eV. Thus, we conclude that the effect of electrons occupying the He-He anti-bonding molecular orbital is negligible.

We also conducted simulations using the time-dependent local density approximation (TDLDA)[35] and again found photo-enhancement of He-He attraction.[36] We thus concluded that photo-induced enhancement of attractive

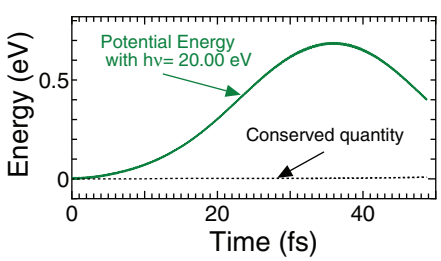

FIG. 4. Energy increase of He dimer under optical field with photon energy of 20 eV. Solid (green) line shows the total energy and the dotted (black) line shows the conserved quantity calculated by using a scheme in Ref. 28.

He-He interaction is a robust result insensitive to the van der Waals correction and to the choice of exchange-correlation functional.

In summary, we have demonstrated enhancement of interatomic attractive interaction by light of constant spatial intensity; this enhancement does not originate from the intensity gradient of the applied optical field (i.e., it is distinct from the optical tweezer effect). Photo-enhancement of interatomic attractive interaction was found for the He dimer under an optical field with polarization vector parallel to the He-He axis. Depending on the frequency of the optical E-field, the total dipole moment $\mathbf{P}(t)$ shows either Rabi oscillation or increased amplitude. By tuning the frequency of light, we can maximize the photo-induced force to over 7 pN on each He atom. Recent advances in laser technology should enable manipulation of atoms, molecules, and clusters by this method. Photo-enhancement of attractive forces between particles will be useful for synthesizing new and novel structures. The control of weak interactions in microelectromechanical systems[37] and nanobiological systems[38] will also be advanced by the photo-enhancement effect. Moreover, applying an optical field with spatially constant intensity to particles manipulated by light or plasmon with a spatial intensity gradient[10,11] would make the particles condensed by enhanced interparticle attractive interaction.

All calculations were performed using the AIST Super-Cloud Generation 2 (ASC-G2) System. Y.M. acknowledges funding from the Strategic Programs for Innovative Research; the Ministry of Education, Culture, Sports, Science, and Technology, Japan; and the Computational Materials Science Initiative (CMSI), Japan; and support from Research Organization for Information Science and Technology (RIST) at Tokyo Office. A.R. acknowledges financial support from the European Research Council Advanced Grant DYNamo (ERC-2010-AdG-267374), Spanish Grant (FIS2010-21282-C02-01), Grupos Consolidados del Gobierno Vasco (IT578-13), and European Commission project CRONOS (Grant No. 280879-2). H.Z. acknowledges financial support from the National Natural Science Foundation of China (NSFC Grant No. 11074176 and NSAF Grant No. 10976019) and support from the Research Fund for the Doctoral Program of Higher Education of China (Grant No. 20100181110080).

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[33]To facilitate observing this effect with ordinary numerical precision for computation, it is convenient to set He-He distance 2.90 Å, larger than the theoretically optimum value near 2.86 Å, to initiate He-He contraction even without an optical field. Then, comparison between contraction speeds with and without optical field can estimate the enhancement of force while minimizing numerical error, even using typical double precision floating point numbers for the numerical computations.
[34]The raw values of the computed forces during the TDDFT-MD simulation fluctuated with a very short period due to fast-electron dynamics; therefore, it is very difficult to take time-averaged forces acting on He ions. Instead, by using a trajectory based on He-He distance, one can estimate effective forces by applying classical Newtonian dynamics. We compared the dynamics of He-He distance with and without optical field; both show parabolic behavior with respect to time. In the case $h\nu = 20.00$ eV, the effective force on a He atom is around 7 pN larger than the effective force without optical field.
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